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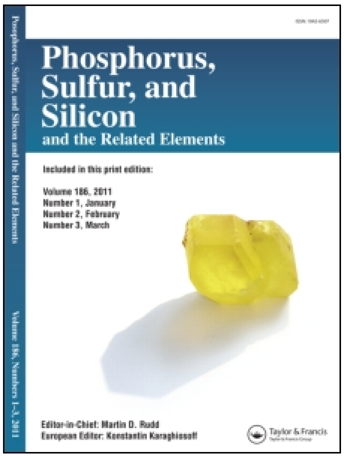

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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ENDOCYCLIC SUBSTITUTION AT TETRACOORDINATE S(VI)

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To cite this Article Andersen, Kenneth K. , Yildiz, Linda J. and Phillips, Brian T.(1979) 'ENDOCYCLIC SUBSTITUTION AT TETRACOORDINATE S(VI)', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 11

To link to this Article: DOI: 10.1080/03086647908080279

URL: http://dx.doi.org/10.1080/03086647908080279

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Phosphorus and Sulfur
1979, Vol. 6, p. 11

Printed in Great Britain

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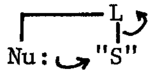
Endocyclic nucleophilic substitution reactions involve molecules in which the leaving group L is attached not only to the site of substitution, "S", but also to the nucleophile, Nu:, by a sequence of atoms in contrast to exocyclic reactions where the leaving group is not attached to the nucleophile. If the substitution reaction is intramolecular as indicated by



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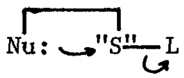
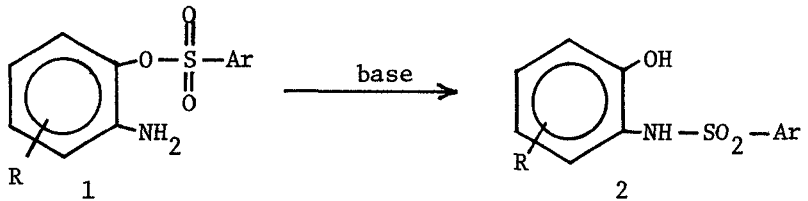


Exocyclic

the drawings, then a change in molecular structure permits a study of the process as a function of the Nu-"S"-L angle.

We investigated endocyclic nucleophilic substitution at tetracoornate sulfur(VI) using derivatives of o-aminophenols (eq. 1). The reactions



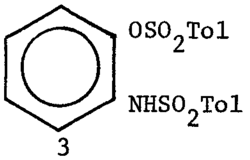
(1)

1 2

proceed intramolecularly and must involve N$-$S(O)$_2$-O angles far from 180°.

If the reaction in eq. 1 proceeded intermolecularly *via* bimolecular reaction of two molecules of 1 (Ar = Tol, R = H), compounds 3 and 4 should have formed but neither was detected. Since 3 was stable under the reaction conditions and did not react with anions derived from 4 to give sulfonamide 2, neither 3 nor 4 was ever produced. We conclude that 2 is formed from 1 by endocyclic nucleophilic substitution.

When a mixture of sulfonates 5 and 6, each separately capable of forming a sulfonamide as in eq. 1, was treated with base, only the two sulfonamides arising from intramolecular substitution were formed, but the two sulfonamides expected from intermolecular reactions between 5 and 6 were not, further supporting the proposed endocyclic mechanism.



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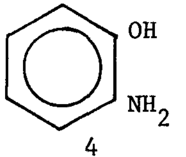

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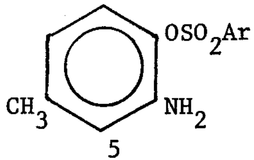

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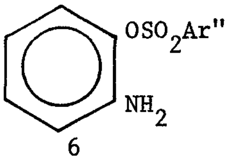

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Additional results will be presented and discussed.